

[54] VOLTAGE STRESS-RESISTANT CONDUCTIVE ARTICLES

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[22] Filed: Dec. 29, 1972

[21] Appl. No.: 319,492

[52] U.S. Cl. 338/22 R, 252/502, 252/511

[51] Int. Cl. H01c 7/04

[58] Field of Search. 338/22 R, 22 SD; 252/502, 252/511; 219/553

[56] References Cited

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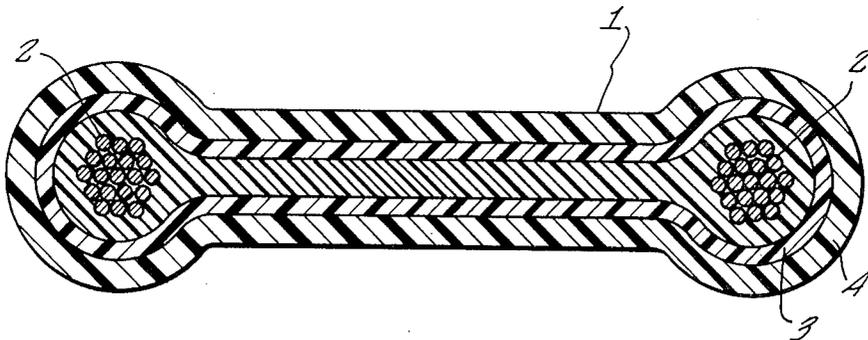
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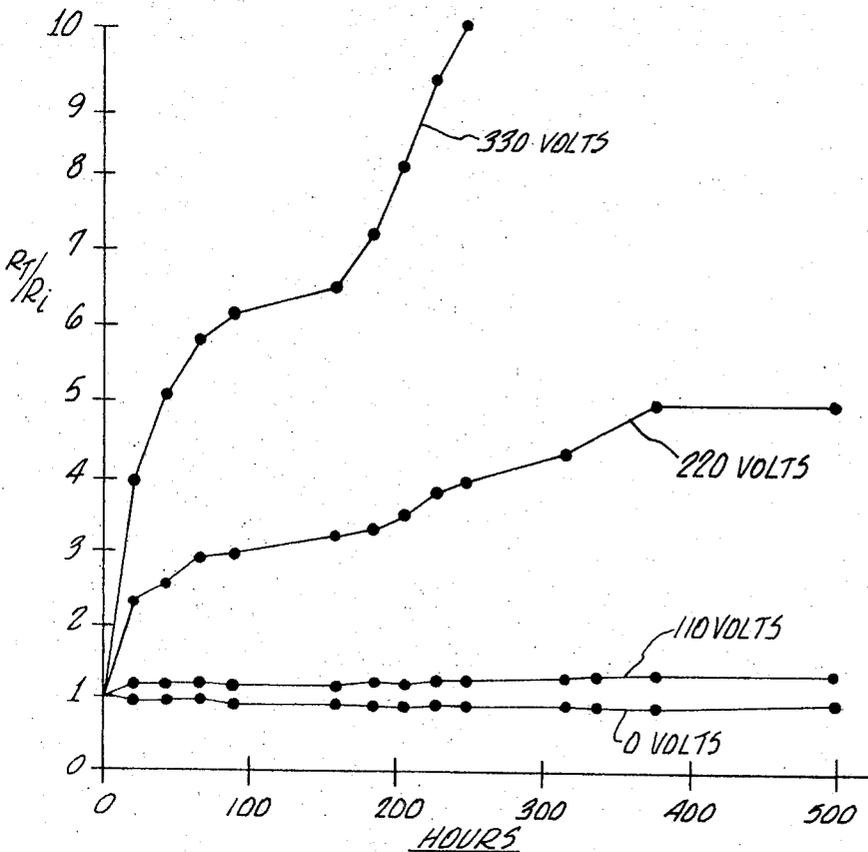
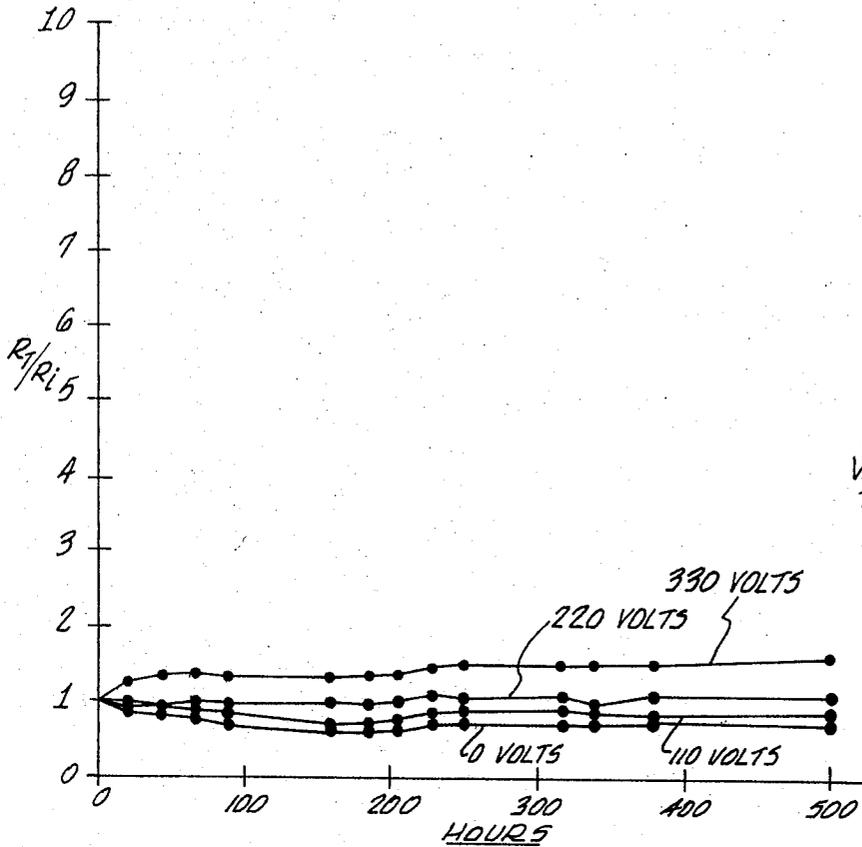
Primary Examiner—C. L. Albritton
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[57] ABSTRACT

Described herein are methods and means by which conductive carbon black-containing resistive heaters which are self-temperature limiting by reason of their positive temperature coefficient of resistance are stabilized against long-term resistance variation under high voltage stress, variously by (a) increasing the proportion of carbon black at the electrode interface relative to that of the remainder of the semi-conductive material of which the article is comprised; and (b) providing at the electrode interface a material selected from the group consisting of carboxylic acid group-containing polymers of acid number greater than 3, their ammonium, alkali or alkaline earth metal salts, or a polymeric amine of amine number greater than 3.

10 Claims, 8 Drawing Figures





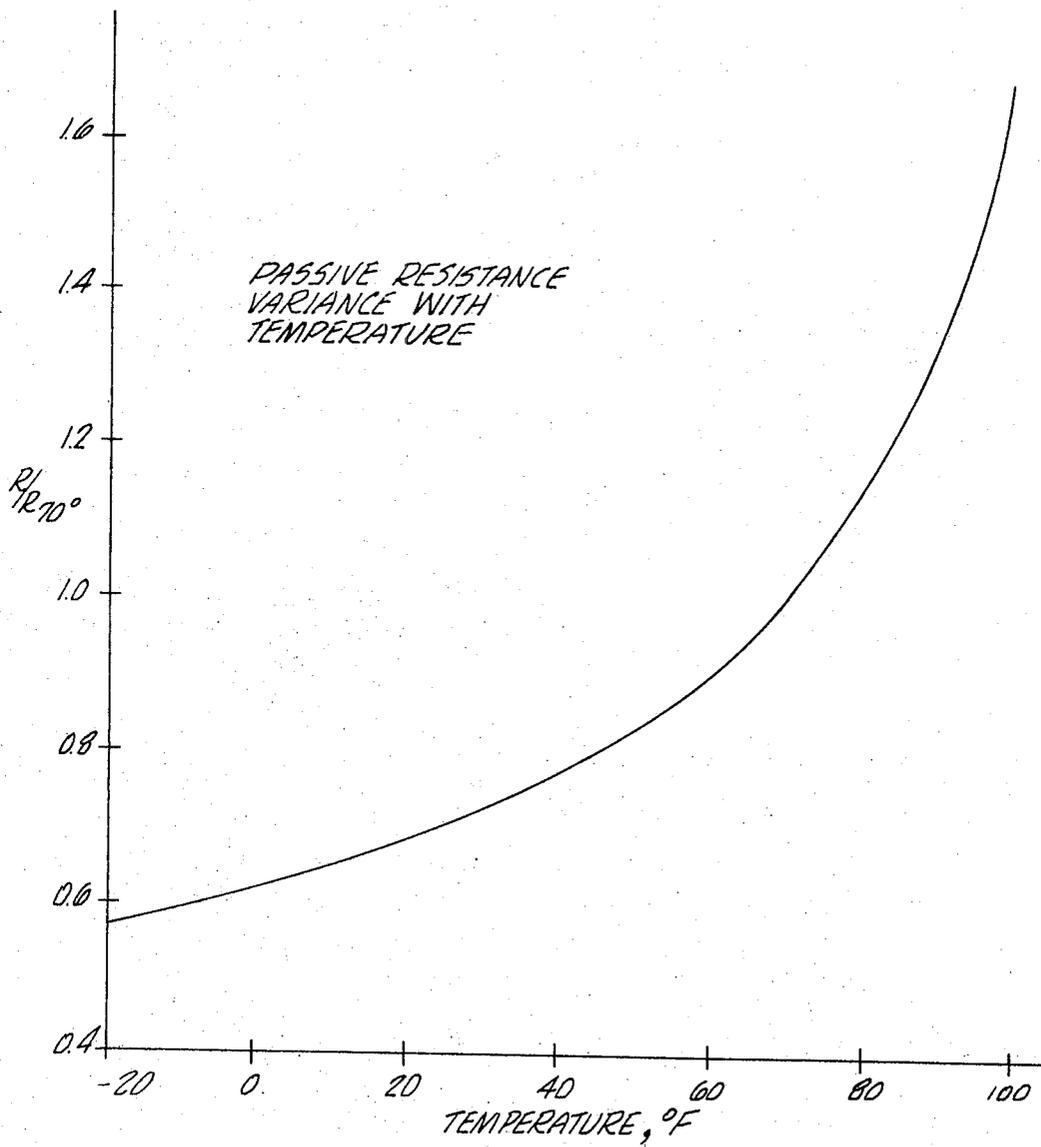
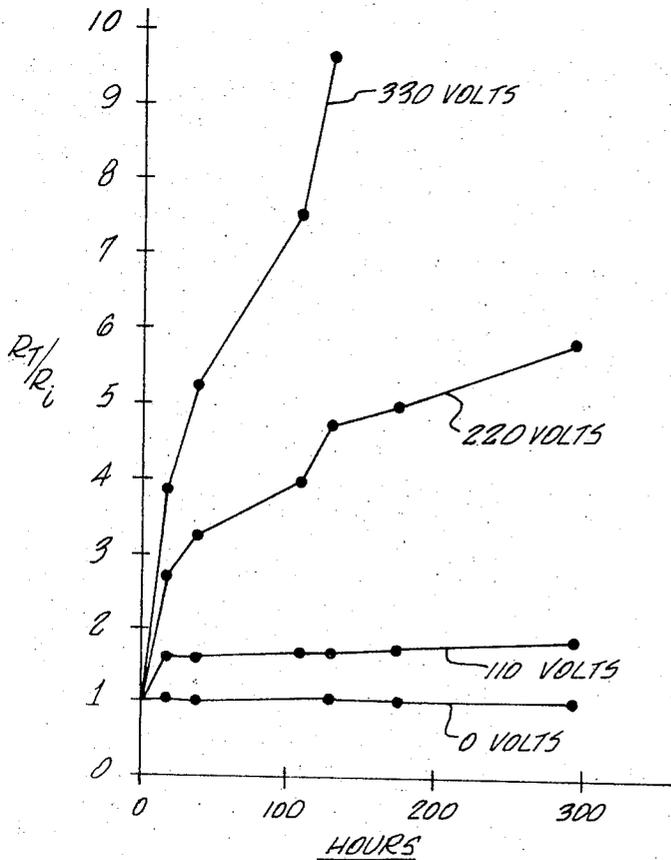
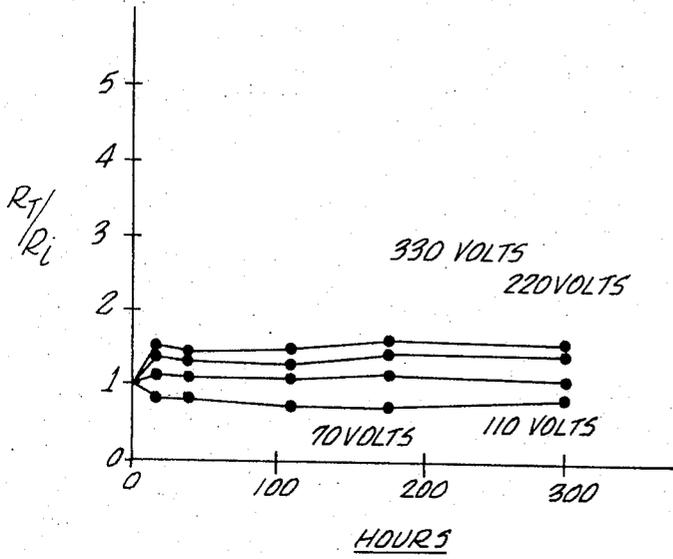


FIG. 3.



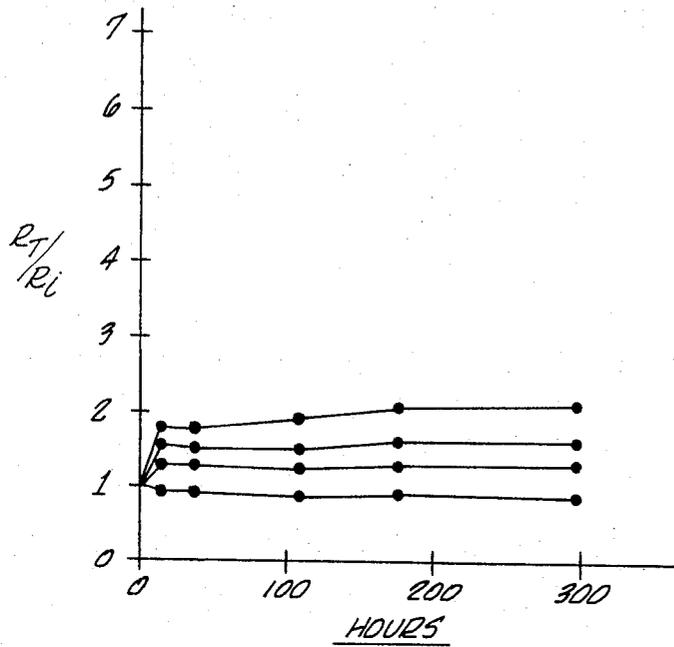


FIG. 6

VOLTAGE INDUCED
RESISTANCE
VARIANCE WITH
TIME (EX. 3)

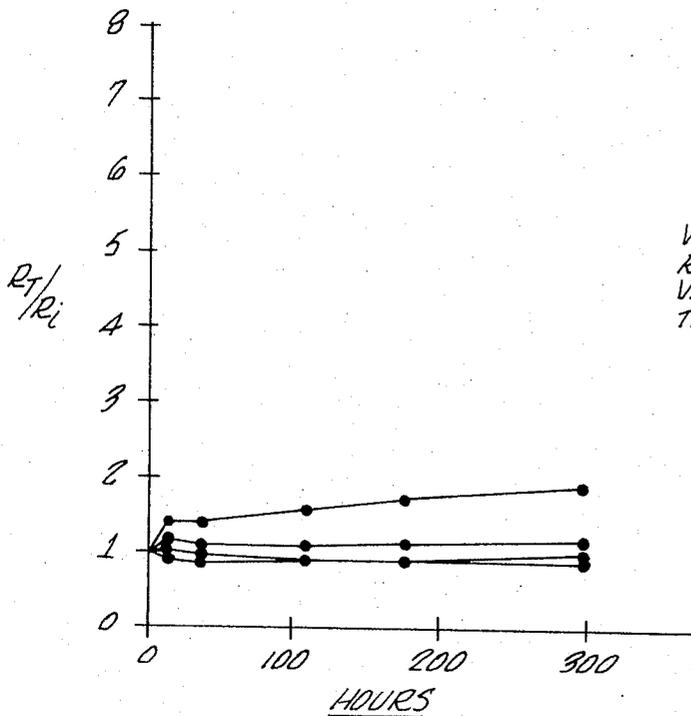


FIG. 7

VOLTAGE INDUCED
RESISTANCE
VARIANCE WITH
TIME (EX. 4)

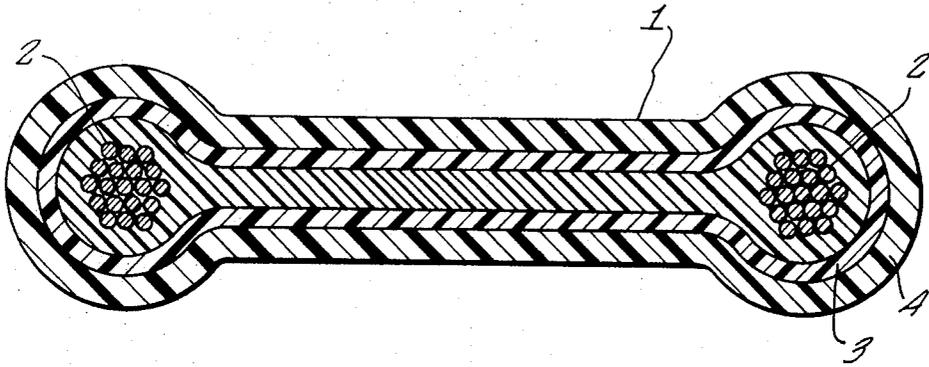


FIG. 8.

VOLTAGE STRESS-RESISTANT CONDUCTIVE ARTICLES

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is related in subject to commonly assigned U.S. Pat. application Ser. Nos. 287,442, 287,443 and 287,444, each filed Sept. 8, 1972.

BACKGROUND OF THE INVENTION

Semi-conductive compositions comprised of conductive carbon black dispersed in an interconnected array of current-carrying channels in a polymeric matrix have heretofore found wide application in resistance heating. Such compositions as exhibit a steep-sloped positive temperature coefficient of resistance have found particular application in the manufacture of self-temperature regulating heating elements, exemplary of which are those described in the aforesaid application Ser. Nos. 287,442, 287,443 and 287,444, the disclosures of which are incorporated herein by reference to illuminate the background of this invention. As the temperature of such a composition increases, either through a rise in ambient temperature or by reason of resistive heating occasioned by the passage of current therethrough, the polymer matrix expands at a rate greater than that of the carbon black particles which, in an interconnected array of channels, impart the property of conductivity. The resulting diminution in the number of current-carrying channels decreases the amount of power generated by I²R heating. This self-limiting feature may be put to work in, e.g., heat tracing pipes in chemical plants for freeze protection, maintaining flow characteristics of viscous syrups, etc. In such applications, articles formed from the conductive composition ideally attain and maintain a temperature at which energy lost through heat transfer to the surroundings equals that gained from the current. If the ambient temperature then falls, increased heat transfer to the surroundings is met by increased power generation owing to the resistivity decrease associated with the article's lowered temperature. In short order, parity of heat transfer and power generation is again attained. Conversely, where ambient temperature increases heat transfer from the conductive article is reduced and the resistivity rise resulting from increased temperature diminishes or stops I²R heating.

Thusfar, the use of self-regulating resistance heating elements has been largely confined to those applications in which operational voltage does not exceed about 110 volts (herein, all voltages are 60 cps, RMS values). However, for employments like heat-tracing pipes in refineries and in other operations in which long runs of resistance-heating strips are desirable, it would be advantageous to reduce line losses by operating at greater voltages. Again, in areas of the world where 110 volt potential is not widely available (particularly in various of the European countries), provision of self-regulating heating elements operable at higher voltage (e.g., at about 220 volts) would be desirable. While the semi-conductive compositions specifically disclosed in the aforesaid commonly assigned applications have proved eminently suitable in heat-tracing applications over periods of many months at 110 volts, when subjected to voltages on the order of 220 volts and higher, we have now found their resistance to increase substan-

tially over periods well within anticipated service life. The problems appears related to the high voltage stress resulting from the confined influence of high operational voltage and the relative contiguity of electrodes employed in heat tracing elements. While we do not wish to be bound by any theory, we believe the disperse nature of conductive carbon in the polymeric matrix surrounding the electrodes and incomplete wetting of the electrode with black-containing polymer, under high voltage stress, creates regions of high localized current density leading to degradation and a concomitant increase of resistance at the interface.

BRIEF SUMMARY OF THE INVENTION

By this invention there are provided methods and means for ensuring long-term resistance stability in self-temperature regulating conductive article subjected to high voltage stresses, and products enjoying that property. According to one embodiment of the invention, the formation of localized regions of high current density at the electrode interface is apparently discouraged by precoating the metallic electrodes with a conductive black-containing composition such that following disposition of the electrodes in spaced-apart relation electrically continuous through a black-loaded polymeric matrix or core (as by extruding the core onto a number of electrodes), the percent by weight conductive black contained at the electrode interface is at least about 1.5 times that of the midpoint between adjoining electrodes. In another embodiment, the objectives of the invention are achieved by uniformly deploying in the matrix or core electrically connecting adjoining electrodes an effective resistance-stabilizing amount of a material selected from the group consisting of carboxylic acid group-containing polymers of acid number greater than about 3, the ammonium, alkali or alkaline earth metal salts of such polymers, and polymeric amines of amine number greater than about 3.

One object of this invention is to secure self-temperature regulating articles which exhibit enhanced resistance to voltage stress-induced resistance variation when powered at high voltage for extended periods.

A further object of the invention is to provide self-temperature regulating conductive articles free from excessive resistance increase upon subjection to high voltage stress early in their service life.

The manner in which these and other objects and advantages of the invention are obtained will appear in greater detail from the description of preferred embodiments and from the accompanying drawings in which:

FIGS. 1 and 2, respectively, graphically depict, for comparison purposes, voltage-induced resistance variance with time in the case of a self-temperature regulating article formed according to one embodiment of this invention and that with a control without the scope of the invention;

FIG. 3 graphically depicts resistance variance with temperature data employed in normalizing resistance values employed in constructing FIGS. 1, 2 and 4-7; and

FIGS. 4, 6 and 7 similarly permit comparison of time-related resistance variation of other embodiments of the invention with control results depicted in FIG. 5.

FIG. 8 is a cross-sectioned end-on view of one jacketed extrudate formed according to the practice of this invention.

DETAILED DESCRIPTION OF THE INVENTION

Ideally, potential drops linearly toward ground across the width of a semi-conductive material electrically connecting two electrodes so that, in the first instance, voltage stress can be considered as the slope of that decrease. With the configurations most commonly heretofore employed in self-temperature regulating heat-tracing articles (i.e., those with specific initial resistivities of about 2,000 ohm-in), where the ratio of voltage to electrode separation in inches has been equal to or greater than about 500, significant resistance increase over long-term powering has been encountered. Of course, the adverse effects of voltage stress will vary inversely with resistivity of the semi-conductive material across which the potential is imposed. Taking q as heat generation (in watts) per cubic inch of a given voltage per inch, $q = V^2/p$, where p is resistivity in ohm-in and V is volts per inch. Where q is greater than about 100.0 watts/inch during operation at 70°F, voltage stress generates resistance degradation. In one aspect of our invention, i.e., that in which polymeric materials containing carboxylic acid or amine functions are disposed in minor proportion of the electrode interface and, preferably, throughout the semi-conductive material electrically connecting adjoining electrodes, it may be that the resulting resistivity stabilization is owed to improved setting of the electrode stemming from the formation of ionic or other bonds between the said functions on the one hand and the electrode on the other. In any event, marked improvement has been had where polymeric amines and acid group-containing polymers like those referred to above have been supplied in the semiconductive composition.

"Amine number", as used herein, refers to that quantity obtained according to the standard ASTM D-2074-66 determination. "Acid number" is the mg. KOH required to neutralize free acid groups contained in 1 gm. of a particular polymer.

Particular preferred carboxylic acid group-containing polymer addends are ethylene-acrylic acid copolymers (preferably the sodium or zinc-neutralized salts thereof such as those sold by E. I. du Pont de Nemours & Company, Inc. under the tradename "Surlyn") and terpolymers of ethylene, vinyl acetate (24-29 percent) and a minor proportion (e.g., = 5 percent) of an α - β ethylenically unsaturated carboxylic acid such as acrylic or methacrylic acid. Exemplary of the latter category is the "Elvax" family of acid terpolymers (acid number of about 6) available from E. I. du Pont de Nemours and Company, Inc. As an example of an especially suitable amine addend may be mentioned poly (2,2,4-trimethyl-1,2-dihydroquinoline) such as that available from R. T. Vanderbilt and Company under the name "AgeRite Resin D."

Generally, significant improvement in resistance stability is obtained where the semi-conductive core electrically connecting adjoining electrodes contains from about 0.1 to about 15, preferably 0.1 to 8 percent, by weight amine or acid additive, based on total weight of the additive-containing semi-conductive material. In the case of poly (2,2,4-trimethyl-1,2-dihydroquinoline), optional results may be obtained with as little as from 0.1 to 2 percent.

In another embodiment of this invention, the adverse effects of voltage stress are diminished by providing the electrodes with a coating containing sufficient carbon black to ensure that at the electrode surface the enveloping conductive material contains at least about 1.5 times that amount of carbon contained at the midpoint between adjoining electrodes where the percent by weight carbon at that midpoint is at least about 9 to 15 percent. Percent by weight carbon at the electrode interface desirably is within the range from about 1.5 to about 7 times that of the midpoint. Most preferably, the electrode coating when dry contains from about 30 to 75 percent by weight carbon black. This differentiation in relative content of carbon is most conveniently achieved by coating onto the electrode a carbon black-rich aqueous composition, preferably one comprised of conductive black in deionized water. The coating composition may optionally contain fillers such as colloidal silica for strength enhancement, etc.

Preferred materials for electrodes include copper, tinned copper, and nickel- and silver-plated copper. The electrodes may vary conventionally in configuration, e.g., flat, round, solid, stranded, etc.

In order to most optimally obtain self-limiting compositions, the polymeric matrix in which conductive black is dispersed in whatever proportion should exhibit overall an appropriately non-linear coefficient of thermal expansion, for which reason a degree of crystallinity is believed useful. Polymers exhibiting at least about 20 percent crystallinity as determined by x-ray diffraction are suited to the practice of the invention. Among the many polymeric matrices with which the invention may be practiced are polyolefins such as low, medium and high density polyethylenes and polypropylene, polybutene-1, poly (dodecamethylene pyromellitimide), ethylenepropylene copolymers and terpolymers with non-conjugated dienes, polyvinylidene fluoride, polyvinylidene fluoride-tetrafluoroethylene copolymers, etc. As is known, blends of polymeric substances may also be employed as the matrices in which the carbon black is dispersed. Typically, the minor polymeric blend component is chosen for superior compatibility with carbon black relative to the blend component present in major proportion, while the latter component is selected for the particular physical properties desired in the overall extrudate. The principal blend component is preferably present in at least about 3:1 weight ratio relative to the minor component with which the black is first mixed. Presently, the blends most preferred have a polyethylene as the principal component, the other being an ethylene-vinyl ester copolymer, such as ethylene-vinyl acetate or ethylene-ethylacrylate copolymers. An especially preferred extrudate contains about 70:20 polyethylene: ethylene-ethyl acetate copolymer by weight. As will be recognized by those skilled in the art, limiting temperatures tailored to the application intended (e.g., freeze protection, thermostating, etc.) may be obtained by appropriate selection of polymeric matrix material. For example, elements which self-limit at temperatures on the order of 100°F, 130°F, 150°F, 180°F and 250°F may be produced with, respectively, wax-poly (ethylene-vinyl acetate) blends, low density polyethylene, high density polyethylene, polypropylene and polyvinylidene fluoride. Other criteria of polymer selection will, in particular instances, include desired elongation, en-

vironmental resistance, ease of extrusibility, etc. as is well known.

The carbon blacks employed are those conventionally used in conductive plastics, e.g., high structure varieties such as furnace and channel blacks. Other conventional addends such as antioxidants, etc. may be employed provided only that their quantities and characteristics do not subvert the objects of the invention. An especially interesting class of beneficial addends are materials such as waxes which, while compatible with the predominant blend component, melt at lower temperature. The result is to permit obtainment of a given wattage at lower temperature, owing to a first peaking effect of the wax on the resistivity-temperature curve. Compounding of the core material intended for extrusion about coated or uncoated electrodes is conventional and generally involves banburying, milling and pelletizing prior to pressure extrusion of the self-limiting element from the melt. Where a polymeric amine or carboxylic acid group-containing polymeric addend is employed as a component of the polymeric matrix material according to one embodiment of the invention, it may be added at any point in compounding of that material.

Preferably, as will appear from FIG. 8, the black-containing matrix 1 is extruded onto a spaced-apart pair of elongate electrodes 2 to form an element rod-shaped or, most preferably, dumbbell-shaped in cross-section, the extruded thermoplastic both encapsulating and interconnecting the electrodes.

To reduce resistivity of extruded product to acceptable initial levels it is preferably annealed at a temperature greater than about 250°F, preferably at least about 300°F, and in any case at or above the melting point or range of the polymeric matrix in which the carbon black is dispersed. The period over which annealing is effected will, it will be appreciated, vary with the nature of the particular matrix and the amount of carbon black contained therein. In any case, annealing preferably occurs over a time sufficient to reduce resistivity of the annealed element to satisfaction of the equation $2L + 5 \log_{10} R \leq 45$, preferably ≤ 40 (L being percent by weight black in the matrix and R resistivity of the extrudate in ohm-cm) and the time necessary in a particular case may be readily determined empirically. Typically, annealing is conducted over a period in excess of 15 hours, and commonly at least about a 24 hour anneal is had. Where the element is held at anneal temperature continuously throughout the requisite period, it is advisable to control cooling upon completion of the anneal so that at least about 1½ hours are required to regain room temperature. However, control of cooling is substantially less important where the requisite overall annealing residence time is divided into at least about 3 roughly equal stages and the element returned to room temperature between each annealing stage.

Because the polymeric matrix of black-containing extrudate is in the melt during annealing, that extrudate is preferably supplied prior to annealing with an insulative extruded jacket 3 (see FIG. 8) of a thermoplastic material which is shape-retaining when brought to the annealing temperature. Suitable jacketing materials are discussed in length in the aforesaid application S.N. 287,442.

Upon completion of annealing and optional addition of a further insulative jacket 4 of, e.g., polyethylene, the self-limiting element is desirably subjected to ioniz-

ing radiation sufficient in strength to cross-link the black-containing core. Radiation dosage is selected with an eye to achieving cross-linking sufficient to impart a degree of thermal stability requisite to the particularly intended application without unduly diminishing crystallinity of the polymer matrix, i.e., diminution of overall crystallinity of the cross-linked black-containing matrix to less than about 20 percent is preferably avoided. Within those guidelines, radiation dosage may in particular cases range from about 2 to 15 megarads or more and preferably is about 12 megarads.

The invention is further illustrated by reference to preferred embodiments thereof in the Examples which follow, in which all parts and percentages are by weight and all temperatures are expressed in Fahrenheit degrees unless otherwise noted.

EXAMPLE 1

A. Preparation of Electrode Coating Composition

To a tank were added, with stirring, 200 lbs. colloidal silica ("Ludox HS-40," E. I. duPont de Nemours & Company, Inc.), 40 lbs. of a 25 percent aqueous solution of Tamol 731 (a sodium salt of a polymerized carboxylic acid available from Rohm & Haas), 60 lbs. dionized water and sufficient ammonium hydroxide to adjust pH to about 9.5.

To a second tank were added, again with stirring, 140 lbs. dionized water and 6 lbs. dicyandiamide-formaldehyde condensate ("Sun Pro 528," available from Sun Chemical Company).

The two masterbatches prepared above were then mixed together under shear for about 15-20 minutes, and the resulting mixture let stand for about 24 hours. Thereafter, 236 lbs. conductive acetylene black (Shawinigan Company) was added to the mixture under shear and the resulting black-loaded composition let stand for a further 24 hour period. Viscosity was then adjusted for optional coating by the addition of about 61 lbs. dionized water.

B. Preparation of Core Material

76 lbs. of polyethylene (density 0.929 gm/cc, 32 lbs. of a mixture of 34 percent Vulcan XC-72 and ethylene ethyl acrylate copolymer (density 0.930 gm/cc, 18 percent ethyl acrylate) were loaded with 1 lb. of antioxidant into a Banbury mixer. The ram was closed and mixing commenced. When temperature reached about 240°-50°F the batch was dumped, placed in a 2-roll mill, cut off in strips and pelletized in a suitable extruder.

C. Extrusion onto Electrodes

Two tinned copper electrodes (20 AWG 19/32) were passed through the coating composition prepared as in Part A above and contained in a recirculant tank to form a coating of about 1 mil thickness and the coating dried by radiant heat. The pelletized material formed in Part B above was then extruded onto two parallel coated electrodes to form an extrudate generally dumbbell-shaped in cross-section. The electrodes were 0.275 inch apart (center-to-center), the interconnecting web being about 15 mils in thickness, at least 8 mils thickness of the semiconductive composition surrounding the electrodes. Extrusion was performed in a plasticating extruder with crosshead attachment (Davis-Standard 2 inch extruder, 24/1 L/D, with PE screw). Thereafter, the same extruder was arranged to extrude an 8 mil thick insulation jacket of polyurethane (Texin 591-A, available from the Mobay Corporation). For

optional geometric conformation, a conventional tube extrusion method was employed in which a vacuum (e.g., 5–20 inch H₂O) is drawn in the molten tube to collapse it about the semiconductive core within about 3 inches of the extrusion head. The jacketed product was next spooled onto aluminum disks (26 inches diameter) and exposed to 300°F for 24 hours in a circulating air oven. Following this thermal structuring procedure, the extrudate was cooled to room temperature over about 1½ hours.

For comparison, a control was prepared following the foregoing procedure save that the core material was extruded about uncoated electrodes. The resistance of a 1 foot section of the control extrudate was measured at various temperatures with a wheatstone bridge, the resulting values divided by measured resistance at 70°, and FIG. 3 prepared from the resulting values.

D. Voltage-Induced Resistance Variance Compared

Three 1-foot lengths of each of the control and electrode-coated extrudates were next respectively subjected to voltages of 110, 220 and 330 volts over an extended period of time. Periodically, the samples were deactivated, cooled to ambient and resistance readings taken with a Weston Digital voltage ohm meter (Model 1240). As an addition control, the resistance of a fourth strip of each extrudate held at zero voltage was periodically determined. The data was then plotted on FIGS. 1 and 2, respectively, for electrode-coated and control extrudates, after normalization to account for variance in ambient resistance measurement temperatures. The normalized resistance at any time R_T (or, at zero time, R_t) was determined by dividing resistance measured at a particular ambient temperature by the coefficient on the ordinate of FIG. 3 obtained at that same temperature.

A comparison of FIGS. 1 and 2 makes plain that the electrode-coated extrudate exhibits stable resistance characteristics under high voltage stress, whereas the control does not. The extrudate prepared according to this invention markedly differs from the control both in terms of resistance stability after extended powering and in freedom from excessive resistance increase in early operational life.

EXAMPLES 2–4

In these examples, voltage stress resistance is enhanced by the addition of acidic or amine polymers to the core material itself without resort to the electrode-coating technique described in Example 1. The following core additives were employed in the proportions stated (based on total weight of core material and addend).

Example	Additive	Percent
2	Surlyn A-1760	5
3	Elvax 4355	5
4	AgeRite Resin D	1

In the case of Examples 2 and 3, 71 lbs. of polyethylene (density 0.929 gm/cc), 32 lbs. of a mixture of 34 percent conductive oil furnace black (Vulcan XC-72, Cabot Corporation) and ethylene ethylacrylate copolymer (density 0.930 gm/cc, 18 percent ethylacrylate) and 1 lb. antioxidant were loaded with additive in the above proportions into a Banbury mixer. In Example 4

the same procedure was followed save that 76 lbs. of polyethylene were employed and the optional antioxidant excluded. In each example, the resulting mixture was mixed, milled, extruded and annealed to form a jacketed heating element as in the "control" of Example 1 (i.e., the electrodes were uncoated). As in Example 1, resistance of each extrudate was periodically measured as the extrudates were subjected to various voltages over a lengthy period, and the result data for Examples 2, 3 and 4 plotted as before, respectively, on FIGS. 4, 6 and 7. FIG. 5 depicts data similarly obtained with a control identical to that of Example 2 save that Surlyn resin was replaced with an equal weight of polyethylene. Just as in the case of Example 1, the plots obtained in Examples 2–4 demonstrate the markedly superior long-term resistance characteristics obtainable according to this invention.

We claim:

1. In an electrically conductive self-regulating article comprised of at least two spaced-apart metallic electrodes electrically interconnected by a composition containing conductive carbon black dispersed in a crystalline polymeric matrix, the improvement wherein voltage-induced resistance variance is diminished which comprises providing at the electrode surface an effective resistance-stabilizing amount of a material selected from the group consisting of carboxylic acid group-containing polymers of acid number greater than about 3 and the ammonium, alkali or alkaline earth metal salts of such polymers.
2. The article of claim 1 wherein said material is selected from the group consisting of zinc and sodium salts of an ethylene-acrylic acid copolymer.
3. The article of claim 2 wherein said material is uniformly dispersed throughout said matrix in the amount of from about 2 to 8 percent by weight based on total weight of the material-containing matrix.
4. The article of claim 1 wherein said material is a terpolymer of ethylene, vinyl acetate and α - β ethylenically unsaturated carboxylic acid.
5. The composition of claim 4 wherein said material is uniformly dispersed throughout said matrix in the amount of from about 2 to 8 percent by weight based on total weight of the material-containing matrix.
6. The article of claim 4 wherein said material is uniformly dispersed throughout said matrix in the amount of from about 0.1 to 2 percent by weight based on the total weight of the material-containing matrix.
7. In an electrically conductive self-regulating article comprised of at least two spaced-apart metallic electrodes electrically interconnected by a composition containing conductive carbon black dispersed in a crystalline matrix, the improvement wherein voltage-induced resistance variance is diminished which comprises providing that the percent by weight conductive black at the electrode surface is at least about 1.5 times that contained in said matrix at the midpoint between adjoining electrodes, the latter constituting at least about 5 percent by weight of the total weight of matrix and conductive black at said midpoint.
8. The article of claim 7 wherein the percent by weight of carbon at said midpoint is within the range from about 9 to about 15 percent.
9. The article of claim 8 wherein the percent by weight of carbon at said surface is from about 30 to about 75 percent.

10. In a electrically conductive self-regulating article comprised of at least two spaced-apart metallic electrodes electrically interconnected by a composition containing conductive carbon black dispersed in a crystalline polymeric matrix, the improvement wherein 5

voltage-induced resistance variance is diminished which comprises providing at the electrode surface an effective resistance-stabilizing amount of poly(2,2,4-trimethyl-1,2-dihydroquinoline).
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